GEOCHEMICAL CORRELATION OF POLYFACIES SEDIMENTS OF THE UPPER PERMIAN OF THE EAST RUSSIAN PLATFORM

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As the direct correlation of marine and non-marine facies of Upper Permian in stratotypical region of eastern part of Russian Platform on the basis of palaeontological and lithological data is impossible, other criteria are required. First attempt of correlation on the basis of geochemical data has been made. Groups of typomorphic elements related to carbonates (Sr, Mn, Ba, Sc, Y) and shales and sandstones (Ga, Ti, Ni, V, Cr, P, Zn, Li, B) are determined. Elements which set up geochemical barriers in transitional environment are determined. An important role of organic matter in accumulation of chalcophile and noble metals is stated. It is proven that geochemically homogeneous carbonate strata can be used as reference points for correlation.

THE VOLGA–URALS region is a type area of the Permian sediments used by Sir Roderick I. Murchison to define the Permian System as such in 1841 (Murchison 1849). In this area, the Upper Permian consists of the Ufimian, Kazanian and Tatarian Stages which unconformably overlie the eroded Lower Permian surface. The carbonaceous terrigenous rocks were defined by S. Nikitin (1887) as the Tatarian Stage using the outcrops from the Vyatka river basin. The reference section of the Tatarian sediments is that of Pechischi. The Kazanian Stage was defined by A. Netschaev (1915), Professor of Kazan University. The underlying red beds were defined as the Ufimian Stage.

The geological structure of the Upper Permian deposits in the Volga–Urals region is featured by facies zonality, caused by transgressive–regressive motion of marine basin at that geological time. Detailed facies studies of marine and continental sediments of the Kazanian conducted by N. Golovkinsky (1868) resulted in determination of its facies changes in time and space.

Upper Permian deposits mainly consist of terrigenous red-beds and carbonaceous terrigenous grey rocks. Lithologically they are represented by sandstones, siltstones, argillaceous and carbonate rocks which were formed in various facies environment. Repeated change in conditions of deposition was accompanied by sharp geochemical contrasts resulting in significant redistribution of chemical components and, as a result, occurrence of favourable conditions for concentration of some elements. Confined to the zone of facies transitions in Volga–Urals region are numerous occurrences of copper metallisation, like cupriferous sandstone, coal deposits (Khassanov & Gafurov 1997), eastwards taking industrial dimensions, and other deposits (bitumen, limestones, decorative stones). Some of them are accompanied by increased concentrations of some chemical elements, which can be of practical interest. The main elements accumulated in such a way are copper, silver and molybdenum. In addition, in a number of cases an increased content of gold, platinum, palladium and germanium was observed in carbonaceous formations. Important for this is organic matter, which is the main concentrator of rare elements. Organic matter of the Upper Permian is represented by plant remains turned into coal confined to the Lower Kazanian, its content increasing considerably in north-east direction. Coal stringers are here up to 0.3 m thick.

The replacement of marine facies by littoral marine ones and by deposits of freshwater ponds took place in an easterly direction. The polyfacies character of the structure of Upper Permian deposits characterised by the absence of extended lithologically uniform strata encumbers significantly their stratigraphic division and correlation. The main difficulty here is the practical complexity of palaeontological comparison of normal marine and limnetic fauna with the entailed lack of precise criteria for determination and correlation of stratigraphic boundaries. This makes of current interest the study of geochemical specialisation and distribution of microelements in the deposits of Upper Permian age on the basis of detailed research of stratotypes and bores. The study of geochemistry of the Upper Permian deposits and, in particular, of distribution of diffuse elements in them can

Fig. 1. Location of studied outcrops in Tatarstan (East Russian Platform).

	Shale			Aleurolite			Sandstone			Carbonate		
	1	2	3	1	2	3	1	2	3	1	2	3
Mn	94	640	961	45	880	1118	198	640	1976	364	2270	2994
	Pb	9	19	14		11	13	25	18	13	10.8	33
7		Ga	3.8	15	15	1	27	15	6	28	15	1.7
7	4		V	4.8	61	148	1	77	149	9.5	93	151
9.9	25	25		Cu	14.8	36	70	5.5	46	62	16.3	46
58	8.8	44	39		Zn	36	110	81	20	110	79	273
120	71	327	10	31		Ti	1600	3500	3009	400	3300	2934
2130	4000	3106	540	600	1160		Ni	49	42	106	7	52
96	31.3	58	85	15.4	24	17		Zr	62	150	86	7
130	82	155	170	87	15	100	76		Cr	31.6	37	183
5	55	185	88.8	67	234	17	18	47		Sr	74	150
74	75	180	69	178	260	73	180	300	181		Ba	58
160	186	100	320	232	105	400	204	56	470	220		Y
18	13	11	17.5	18	12	23.8	14	13	20.4	2	12	

Table 1. Mean contents of microelements (ppm) in Upper Permian outcrops: 1, Pechischi; 2, Vandovka; 3, Sentyak (Lower Tatarian + Upper Kazanian).

considerably assist at issues of their local, regional and interregional correlation, division and facies analysis.

We investigated the stratotype and reference sections of the Upper Permian (outcrops Pechischi, Vandovka, Sentyak, Elabuga, Prosti) placed across the facies zones from Kazan to Elabuga (Fig. 1). The main sections are shown in Fig. 2. The results obtained were used by the authors for geological mapping at 1:50 000 scale conducted on the territory of Tatarstan Republic.

The conducted research has revealed two main groups of elements, characteristic for various lithological formations: carbonaceous and carbonaceous–terrigenous (mollasoid). Mean contents of microelements in rocks of the formations in the stratotypes are presented in Table 1.

Typical for the carbonaceous formation are

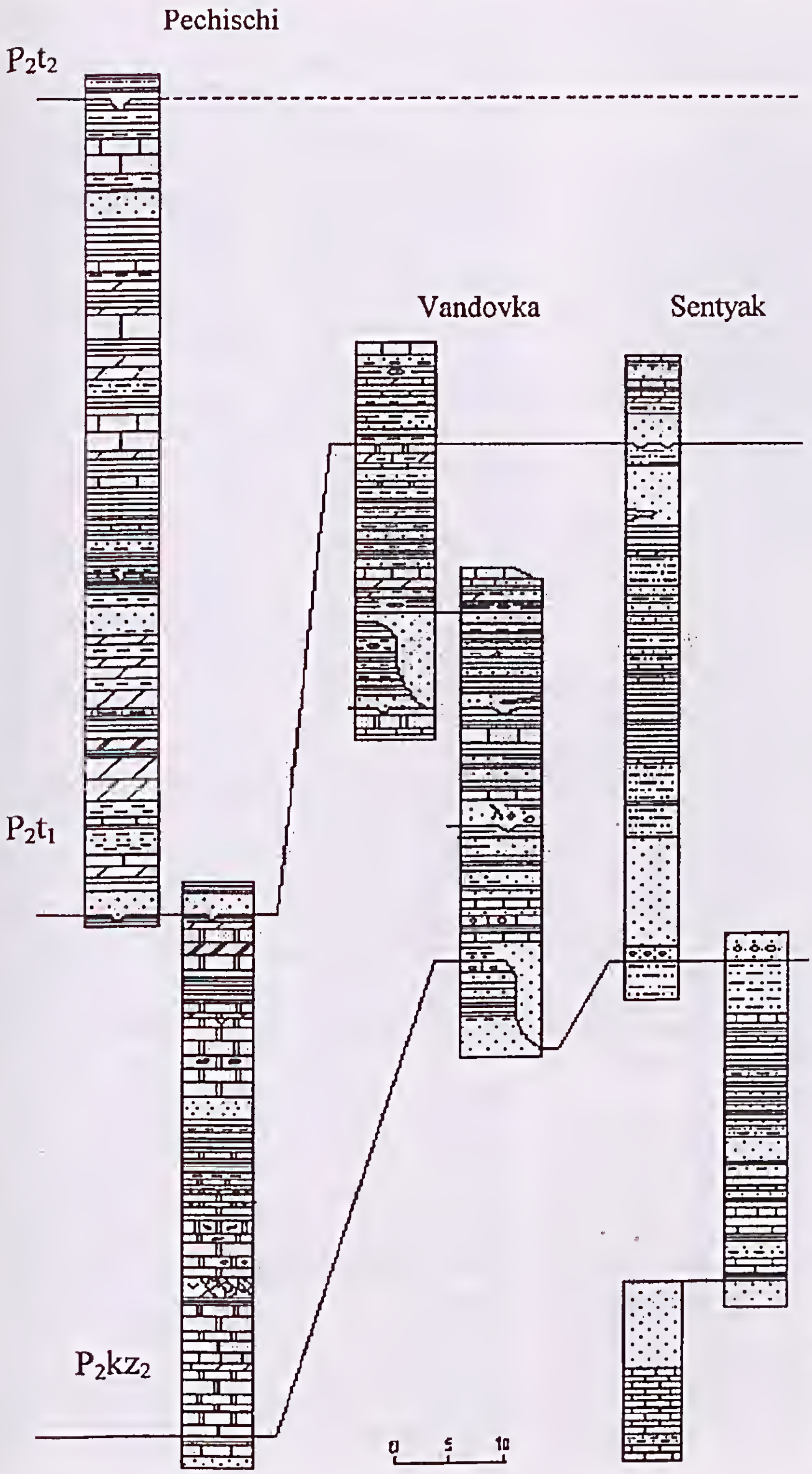

Fig. 2. Sections of Upper Permian outcrops in the East Russian Platform: P_2t_2, Upper Tatarian; P_2t_1, Lower Tatarian; P_2kz_2, Lower Kazanian.

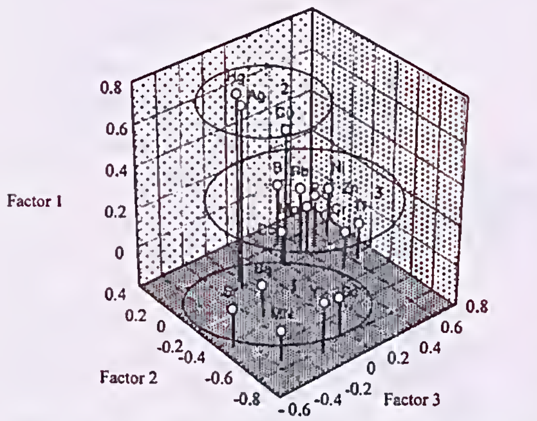

Fig. 3. Factor diagram for elements of Upper Permian: 1, limestone; 2, geochemical barriers; 3, terrigenous complex.

Sr, Mn, Ba, Sc, Y, which are mainly concentrated in carbonaceous minerals, while for the mollasoid formation specific are Ga, Ti, Ni, V, Cr, P, Zn, Li, B, present in terrigenous material. A third group of elements (Cu, Ag, Hg) is characterised by its own peculiar behaviour which serves as an indicator of geochemical barriers in the transitional littoral-marine facies zone (Fig. 3). The occurrence of geochemical barriers is mainly determined by the presence of a great deal of organic matter, which builds reducing sulphuretted hydrogen environment. In coal of the Kazanian stage, connected with the transition zone from marine facies to littoral-marine ones, in the vicinity of outcrops of Sentyak, Elabuga, were observed increased contents of Pt up to 1.3 ppm, Ag up to 34 ppm, Au up to 20 ppb, Ge up to 170 ppm.

Each of the three groups of elements is indicative of specific geochemical trends. Thus, the 'carbonaceous group' sharply distinguishes carbonates of both marine and non-marine origin within homogeneous argillaceous-sandstone stratum. Carbonates are also distinguished by a complex of additive and multiplicative factors for opposite groups of elements—'carbonaceous' and 'terrigenous' (Fig. 4). It is very likely to be connected with authigenic origin of carbonaceous rocks, geochemical features being determined by specific chemical environment and depth of the basin of sedimentation. The Kazanian limestones were found to be geochemically different from those of the Tatarian. The former are characterised by increased contents of Sr, Cu, Mo, B, Cr, and values of Cu/Ag, Cu/Ti, B/Ga, while the latter by increased contents of Mn and Cr/B ratio. The difference between the Kazanian and Tatarian carbonates is connected with the distinction of environments in basins of carbonatogenesis; Kazanian carbonates have been formed in open marine basin, whereas the Tatarian carbonates were formed in closed lagoon or lakes.

An expressed tendency in decrease of absolute concentration of strontium and increase of content of manganese from west to east was observed, which is connected with general desalination of the basin in the direct vicinity from coastal lines. At the same time, in a vertical profile of the Upper Permian the decrease in content of Sr and Sr/Ba ratio and increase of concentration of Mn is observed in carbonates (Fig. 5). The tendency of desalination of isolated basins of Tatarian stage is reflected in geochemical profile of rocks and is consistent with palaeontological data. Entry forms in carbonates of Li, Ti, Ni, V, Cr, B, Ga are connected with clastic and argillaceous components, so their role in the same directions increases.

In the continental red-beds of the Upper Permian, geochemical markers are exhibited due to maximum contents of elements of Fe group. In particular, according to an additive factor which includes Ti, Ga, V, Cr, Li and Zn stand out beds of basal sandstones and shales. Upwards from the Ufimian to Tatarian stages in the argillaceous-sandstone red-beds, the concentrations of Mn, Ga, V, Cu and V/Ti, Cr/B ratios increase, while the concentrations of B, Li, Ba and Mn/Ba, B/Ag, B/Ga decrease. These geochemical features can assist in determination of stratigraphic units in palaeontologically barren terrigenous strata, fixing on the basis of multiplicative factors changes in conditions of sedimentogenesis. It must be noted that the one-element criterion here does not allow to make divisions of uniform continental strata. Advanced statistical techniques were used for obtaining the criteria (additive and multiplicative factors, factor and cluster analysis). Geochemical reducing barriers are fixed by contrast anomalies of chalcophile elements at transition 'continent-sea' and 'sea-continent'. The argillaceous band containing *Lingula orientalis* (Gol.) was determined by A. Nechaev (1915) to be the bottom of the Kazanian. For the first time here, a Hg-anomaly of 2.7 ppm was recorded. Anomalies of Cu are responsible for a reverse transition from marine to continental sediments within the Kazanian stage. Marine Kazanian sediments are distinguished from underlying and overlying continental sediments by anomalies of Ag.

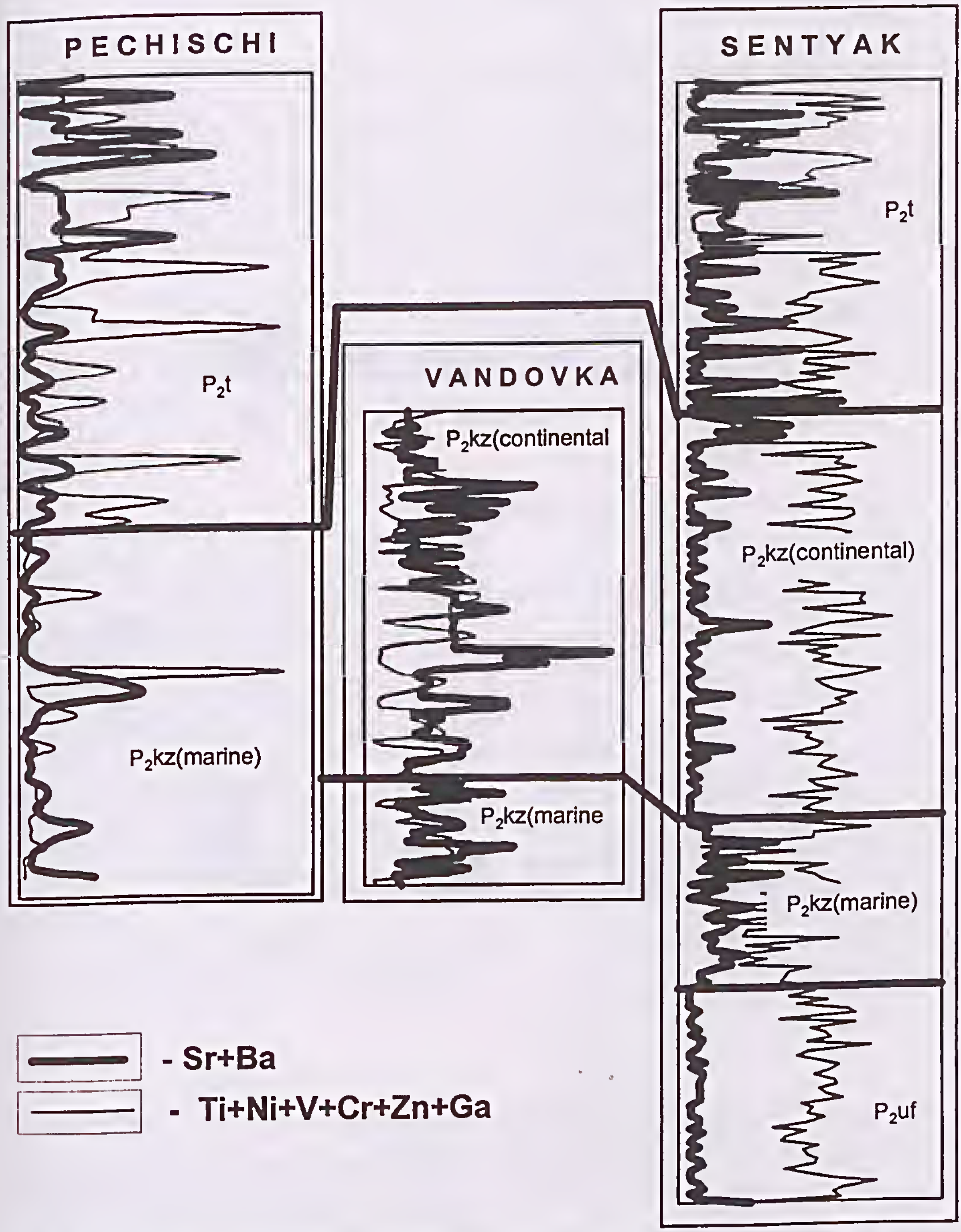

Fig. 4. The regional geochemical correlation of Upper Permian outcrops in the East Russian Platform: P_2t, Tatarian; P_2kz, Kazanian; P_2uf, Ufimian.

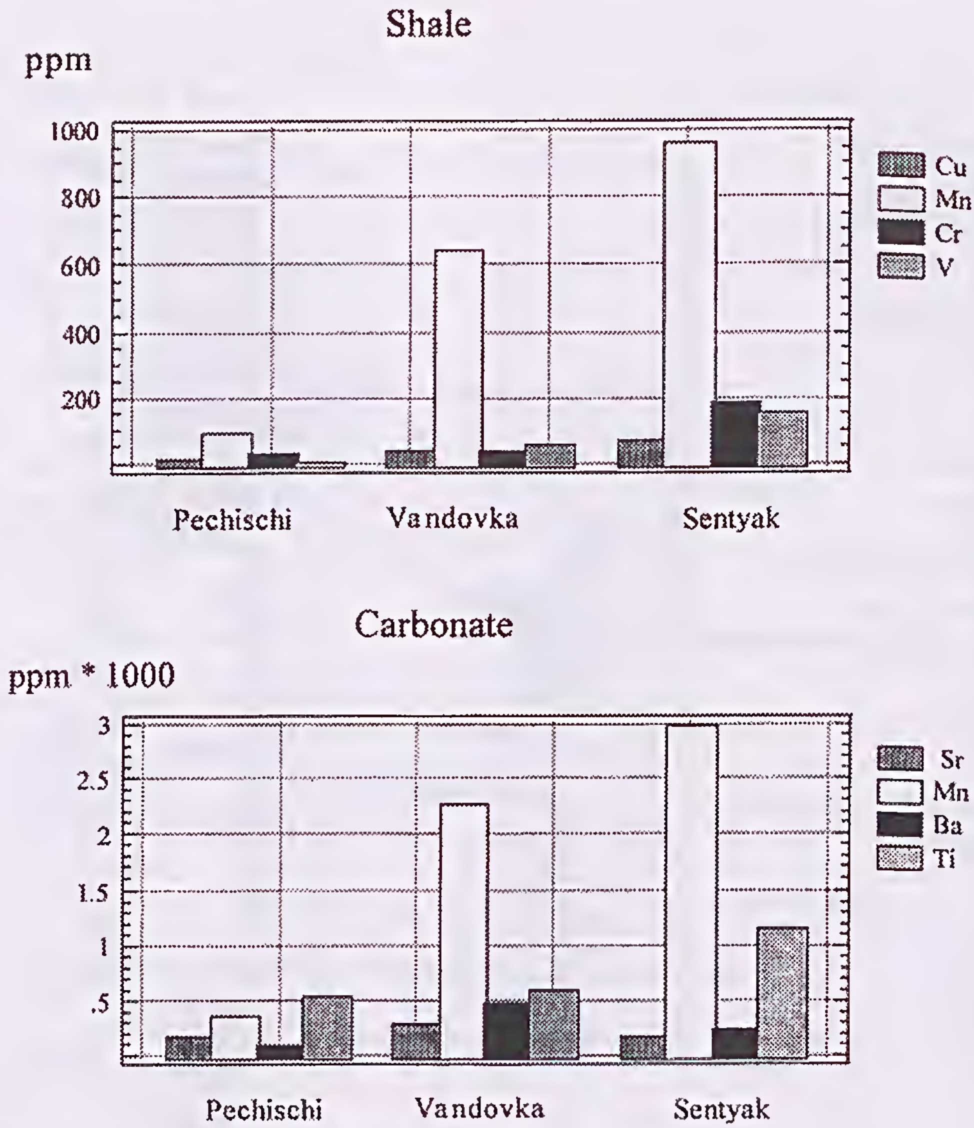

Fig. 5. Diagram of mean contents (ppm) of elements in Upper Permian.

Statistical analysis of spectral data for separate types of rock has been performed. The main types of rocks participating in Permian deposits were considered: shale, siltstone, sandstone, carbonate rock (limestone and dolomite). As a result of the analysis the existence of specific geochemical characteristics for each of the types is revealed and geochemical distinction between rocks of different stages within the lithological types is established.

The discriminant analysis (Khassanov & Novikov 1997) was also used to reveal geochemical distinctions of lithological types. The main types of Permian deposits considered were clays, aleurolites, sandstones and carbonates (limestones and dolomites). Geochemical criteria for distinction of the

	Shale	Sandstone	Aleurolite	Carbonate
Shale	251	77	79	21
Sandstone	61	154	61	13
Aleurolite	79	83	122	10
Carbonate	30	5	8	84

Table 2. Classification matrix for Upper Permian rocks.

	P_2t	P_2kz_1	P_2kz_2	P_2uf	P_1sak
P_2t	15	3	2	0	0
P_2kz_1	2	19	2	0	1
P_2kz_2	2	2	28	0	2
P_2uf	0	0	0	1	0
P_1sak	2	0	0	0	46

Table 3. Classification matrix of carbonaceous rocks for stages of Upper Permian: P_2t, Tatarian; P_2kz_1, Upper Kazanian; P_2kz_2, Lower Kazanian; P_2uf, Ufimian; P_1sak, Sakmarian.

types were found. The results of classification due to geochemical features are shown in Table 2, the rows of which correspond to the real types of specimens, and the columns to the class of specimens resulted from the discriminant analysis.

In addition, it was found that the rocks of different ages but of the same lithological types are geochemically significantly different, enabling their correlation using geochemical logs of different boreholes and outcrops. It must be noted that the most reliable results are those for carbonate rocks. The results of classification of carbonate specimens by the method of simple discriminant functions of Fisher are presented in Table 3, where the rows correspond to the real age of the rock, and the columns to the classification given by the algorithm.

For terrigenous rocks, this distinction is expressed to a lesser extent, as their formation was accompanied by multiple redegradation and redeposition.

CONCLUSIONS

1. For the first time we have established geochemical features of rocks of different stratigraphical divisions of the Upper Permian at the stratotypical region of the Upper Permian in the eastern part of the Russian Platform. It was possible to reveal elements, connected with carbonaceous rocks, sandstones, shales, and to trace a change in their content along the direction of facies changes. A group of chalcophile elements, accumulations of which occur at a boundary between facies, was also revealed.
2. The results of our investigations allow to recommend carbonate strata possessing specific features (special durability, fauna residuals, geochemical features) as correlative markers and show the possibility, in principle, of local geochemical correlation of polyfacies of the Upper Permian.
3. Geochemical barriers, comprising organic matter, play an important role in commercial accumulations of some chalcophile elements and noble metals.

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